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EOP & EP PROCESS FOR BLEACHING OF CHEMICAL PULP

RELATED APPLICATION

This application claims priority from Provisional Application Serial Number 60/271,987 filed on February 27, 2001.

BACKGROUND OF THE INVENTION

Historically the treatment of wood chips to form a chemical pulp has been divided into two processes. The first process is pulping and the second process is bleaching.

Pulping is the changing of wood chips or other wood particulate matter to fibrous form. Chemical pulping includes partial removal of lignin and other materials associated with the wood.

Bleaching is the treatment of the partially delignified cellulosic fibers with chemicals to remove or alter the coloring matter associated therewith. Bleaching brightens the fibers in order to reflect white light more truly.

Throughout the evolution of pulp bleaching, caustic soda (NaOH) has been used as the primary alkali source in bleaching of chemical pulp. Caustic soda is a highly soluble alkali that readily provides an optimum reaction pH and facilitates the dissolution of lignin from pulp in pulp bleaching. Since caustic soda is a strong base, carbohydrate degradation can occur resulting in a decrease in pulp viscosity and an increase in chemical oxygen demand (COD).

In conventional pulp bleaching, a D- E_{op} -D- E_{p} -D bleaching sequence is often employed for brightening chemical pulp. E_{op} bleaching typically utilizes hydrogen peroxide, oxygen, caustic soda and magnesium sulfate as the bleaching chemicals. E_{p} bleaching typically utilizes hydrogen peroxide and caustic soda as the bleaching chemicals. Conventional E_{op} and E_{p} bleaching suffer from the drawback of increased COD which is described above.

Accordingly, there is a need for a E_{op} and E_{p} bleaching sequences which overcome the above-described drawback.

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SUMMARY OF THE INVENTION

This invention is directed to an E_{op} and an E_{p} process for bleaching chemical pulp which overcome drawbacks associated with conventional bleaching.

The subject process comprises providing a bleached chemical pulp produced by bleaching sequences in which E_{op} and/or the E_{p} aqueous bleaching solutions employed therein include magnesium hydroxide in place of a substantial portion of the NaOH, and as a total replacement for any magnesium sulfate. The E_{op} aqueous bleaching solution can comprise a peroxide compound, an oxygencontaining material, sodium hydroxide and magnesium hydroxide, in the absence of magnesium sulfate. Alternatively, the E_{op} aqueous chemical solution for bleaching chemical pulp can comprise an E_{op} aqueous bleaching solution consisting essentially of a peroxide compound, an oxygen-containing material, sodium hydroxide and magnesium hydroxide. In any case, chemical pulp is bleached with an E_{op} aqueous bleaching solution to form an E_{op} bleached chemical pulp. The E_{op} aqueous bleaching solution of this invention can be employed in a D-E_{op}-D-E_p-D bleaching sequence. The subject invention is also directed to a bleaching sequence which includes the E_p bleaching of chemical pulp. The E_p aqueous bleaching solution can comprise a peroxide compound, sodium hydroxide and magnesium hydroxide, in the absence of magnesium sulfate. Stated another way, an E_p aqueous bleaching solution can be provided consisting essentially of a peroxide compound, sodium hydroxide and magnesium hydroxide. In certain bleaching sequences, for example, the E_p aqueous bleaching solution of the subject invention can be provided for bleaching E_{op} bleached pulp to form an E_p bleached chemical pulp. The E_p aqueous bleaching solution of this invention can also be employed in a D-E $_{op}$ -D- E_{p} -D bleaching sequence.

In the E_{op} and/or E_p processes of the present invention, the amount of sodium hydroxide in the E_{op} and/or aqueous bleaching solution is preferably not more than about 8 % by weight, more preferably not more than about 5 % by weight, and most preferably not more than about 3 % by weight, based on the O.D. weight of said chemical pulp.

Furthermore, the ratio of sodium hydroxide to magnesium hydroxide in said E_{op} aqueous bleaching solution is not more than about 5:1 (based on an OH molar ratio), preferably not more than about 3:1 (based on an OH molar ratio), and most preferably not more than about 1:2 (based on an OH molar ratio). As for the ratio of sodium hydroxide to magnesium hydroxide in said E_p aqueous bleaching solution, it is not more than about 1:1 (based on an OH molar ratio), preferably not more than about 1:3 (based on an OH molar ratio). Most preferably about 100% magnesium hydroxide is employed without substantially any sodium hydroxide.

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Both the E_{op} and E_p bleaching processes of this invention preferably contemplates that the pulp viscosity of a final bleached chemical pulp is at least substantially the same as the pulp viscosity of a final bleached chemical pulp which is bleached with the same total amount of an E_{op} aqueous bleaching solution comprising a peroxide compound, oxygen-containing material, sodium hydroxide, with or without magnesium sulfate, in the absence of magnesium hydroxide, on the one hand, and/or an E_p aqueous bleaching solution comprising a peroxide compound and sodium hydroxide, with or without magnesium sulfate, in the absence of magnesium hydroxide, on the other hand. Pulp viscosity is measured in centipoises using the 0.5% CED viscosity test method described in TAPPI T-230.

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Also, the preferred E_{op} process generates a bleach effluent which has a COD which is less than the COD of a bleach effluent from an E_{op} process which employs an E_{op} aqueous bleaching solution comprising the peroxide compound, oxygen-containing material, sodium hydroxide, with or without magnesium sulfate, in the absence of magnesium hydroxide. More specifically, the COD of the bleach effluent produced using the E_{op} aqueous bleaching solution of the present invention is preferably at least about 5%, more preferably at least about 8%, and most preferably at least about 10%, less than the COD generated by an E_{op} stage which uses an E_{op} aqueous bleaching solution comprising said peroxide compound, oxygen-containing material, sodium hydroxide, with or without magnesium sulfate, in the absence of magnesium hydroxide. COD is measured in mg/L using a HACH test kit.

Moreover, the bleached chemical pulp of a bleach sequence containing the subject process preferably has a final ISO brightness (% ISO) of which is at least substantially the same as the final ISO brightness (% ISO) of bleached chemical pulp which is bleached with the same bleach sequence but with an E_{op} aqueous bleaching solution comprising a peroxide compound, oxygen-containing material, sodium hydroxide, with or without magnesium sulfate, in the absence of magnesium hydroxide, on the one hand, and/or an E_p aqueous bleaching solution comprising a peroxide compound and sodium hydroxide, with or without magnesium sulfate, in the absence of magnesium hydroxide, on the other hand. ISO brightness is measured using the test method described in TAPPI T-452.

The process of this invention also produces a bleached chemical pulp having a preferred wet zero span tensile strength which is at least substantially the same as the wet zero span tensile strength of bleached chemical pulp which is bleached with the same total amount of an E_{op} aqueous bleaching solution comprising a peroxide compound, oxygen-containing material, sodium hydroxide, with or without magnesium sulfate, in the absence of magnesium hydroxide, on the one hand, and/or an E_p aqueous bleaching solution comprising a peroxide compound and sodium hydroxide, with or without magnesium sulfate, in the absence of magnesium hydroxide, on the other hand. Wet zero span tensile strength is measured in km using a Pulmac wet zero-span tensile apparatus.

 E_{op} and E_p bleaching are typically part of a broader overall chemical pulp bleaching sequence. Thus, there can be one or more additional chemical pulp bleaching stages that occur prior to E_{op} and E_p bleaching, as well as one or more additional chemical pulp bleaching stages that occur subsequent to E_{op} and E_p bleaching. Usually, these additional chemical pulp bleaching stages are conducted employing conventional bleaching technology utilizing bleaching chemicals such as ClO_2 , O_2 , Cl_2 and peroxide.

The foregoing and other objects, features and advantages of the invention will become more apparent from the detailed description of a preferred embodiment of the invention below which proceeds with reference to the accompanying drawings.

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DESCRIPTION OF THE DRAWINGS

- FIG. 1 is a schematic diagram comparing pulp brightness for various levels of bleaching solution in an E_{op} bleaching process.
- FIG. 2 is a schematic diagram comparing pulp viscosity for various levels of bleaching solution in an E_{op} bleaching process.
- FIG. 3 is a schematic diagram comparing pulp wet zero-span tensile strength for various levels of bleaching solution in an E_{op} bleaching process.
- FIG. 4 is a schematic diagram comparing pulp COD for various levels of bleaching solution in an E_{op} bleaching process.

DETAILED DESCRIPTION OF THE PRESENT INVENTION

As set forth in Tables I-III, an aqueous slurry containing magnesium hydroxide was employed as a partial substitution for caustic soda and a complete replacement for magnesium sulfate in the extraction-oxygen-peroxide stage (E_{op}) of the bleaching of northeast softwood kraft pulp. More specifically, laboratory experiments examined the bleachability of the pulp through a complete $DE_{op}DE_{p}D$ bleach sequence with complete replacement of magnesium sulfate and partial substitution of NaOH on an OH molar basis using CellGuard OP (see description of CellGuard OP below) in the E_{op} stage. Three magnesium hydroxide substitution levels were evaluated in the E_{op} stage: 0%, 25%, and 50% of the OH derived from CellGuard OP and the balance from NaOH.

In Table III, an aqueous slurry containing magnesium hydroxide was also employed as a partial substitution for caustic soda and a complete replacement for magnesium sulfate in the extraction-peroxide stage (E_p) of the bleaching of northeast softwood kraft pulp. More specifically, laboratory experiments examined the bleachability of the pulp through a complete $D E_{op} D E_p D$ bleach sequence with complete replacement of magnesium sulfate and partial substitution of NaOH on an OH molar basis using CellGuard OP (see description of

30 CellGuard[™]OP below) in both the E_{op} and E_p stages. Four magnesium hydroxide

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substitution levels were evaluated in the E_p stage: 0%, 25%, 50%, 75% and 100% of the OH derived from CellGuard OP and the balance, if any, from NaOH.

Bleaching experiments for the E_{op} stage were performed in a 2-liter, medium consistency oxygen reactor equipped with a mixer. The oxygen reactor was treated with nitric acid to passivate the surface to avoid contamination from metals. The D_0 , D_1 , E_p , and D_2 stages were performed by traditional bag bleaching methods. The brownstock kraft pulp to be bleached had a kappa number of 29.2, a brightness of 26.9% ISO, and viscosity of 48.0 cps. This kraft pulp was bleached under the conditions outlined in Tables I-III. Chemical dosages were based on the weight of oven-dried pulp. The experimental procedure for each stage is summarized as follows:

 $\underline{D_0$ Stage. Standard conditions as set forth in Tables I-III were employed for the D_0 stage. The kappa factor was adjusted with 2.44% ClO₂ to reach the desired kappa number out of the D_0 stage. The pulp was then washed to pH 7.5.

E_{op} Stage. After the D₀ stage, the pulp was extracted with a conventional E_{op} stage which employed 1.7% NaOH and 0.1% MgSO₄. For comparison purposes in Tables I and II, bleaching experiments using CellGuard[™]OP as a replacement for MgSO₄ and as a partial substitute for NaOH were conducted. Caustic soda replacement was based on an OH molar basis. For example, at 25% substitution where 25% of the OH comes from Mg(OH)₂, the respective alkali dosages used were 1.275% NaOH and 0.31% CellGuard OP. Caustic soda contains 42.51% by weight OH ions while magnesium hydroxide contains 58.32% by weight OH ions. For the E_{op} stage in Tables I-III, bleaching occurred at 138 kPa of O₂ pressure for 20 minutes followed by bleaching at atmospheric pressure for the remaining 40 minutes.

Martin Marietta Magnesia Specialties, LLC is the manufacturer of CellGuard[™]OP Magnesium Hydroxide Slurry for use in pulp bleaching. The CellGuard[™]OP Magnesium Hydroxide Slurry, which is produced from a dolomitic lime and magnesium brine process, contains 62% by weight Mg(OH)₂ solids suspended in water. The purity of the magnesium hydroxide is over 98% with low levels of transition metals. This product has a fine particle size (3 microns as

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measured by Micromeritics Sedigraph 5100) which promotes high reactivity and excellent suspension stability.

TABLE I – CONDITIONS FOR EACH BLEACHING STAGE										
Stage	Pulp Tim Consistency %		Temp Pressure (*C) (kPa)		Chemical % on O.D. pulp					
D_0	12	45	60		2.44% ClO ₂					
E_{op}	12	60	70	138 kPa of O ₂ for 20 min, then atm	0.5% H ₂ O ₂ 1.7% NaOH or Mg(OH) ₂ /NaOH 0.1% MgSO ₄ (for Control only)					
$\overline{\mathbf{D}_1}$	12	180	80	***	1.2% ClO ₂					
E _p	12	40	70		0.15% H ₂ O ₂ 0.5% NaOH					
D_2	12	100	80		0.6% ClO ₂					

5 D₁-E_p-D₂ Stages (Tables I and II)-Standard conditions were employed for the D₁-E_p-D₂ stages shown in Tables I and II. The pulp and filtrate following each bleaching stage were tested for ISO brightness and end pH, respectively. The pH of the residual liquor was determined using a pH meter and appropriate buffer solutions to calibrate the pH meter. Pulp samples from the E_{op}, D₁, and D₂ stages were tested for viscosity and wet zero-span tensile strength. The respective filtrates were analyzed for chemical oxygen demand (COD).

After the D_0 stage and washing step, the kappa number decreased from 29.2 to 11.9. Pulp brightness increased from 26.9% ISO to 35.9% ISO. The effects of CellGuard OP substitution in the E_{op} stage on each of the pulp parameters were measured. Table II contains a summary of results for each bleaching test performed.

FIG. 1 compares pulp brightness for the various levels of CellGuard[™]OP substitution in the E_{op} stage. The data shows the increasing trend in brightness with each subsequent bleaching stage for all substitution cases. The control sample, which employed 100% OH⁻ from NaOH (or 0% OH⁻ from CellGuard[™]OP)

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and MgSO₄, yielded an increase in brightness from 62.1% ISO after the E_{op} stage to a final pulp brightness of 90.8% ISO after the D_2 stage.

At 25% substitution with CellGuard $^{\text{M}}$ OP in the E_{op} stage, brightness after this bleaching step (60.1% ISO) was lower than the control. However, equivalent final pulp brightness after the D_2 stage resulted in 90.5% ISO at the same ClO₂ and H_2O_2 charge in the D_1 and E_p stages respectively as the control sample.

At 50% substitution with CellGuard OP, Figure 1 shows that the brightness after the E_{op} stage was 59.7% ISO. Even with the use of a mild alkali in the extraction stage which lowers the bleaching pH to 10.1 for 25% substitution and 9.3 for 50% substitution, comparable final brightness was achieved as evidence by the final 89.9% ISO brightness result after the D₂ stage.

At the end of the E_{op} stage, the control sample yielded a pulp viscosity of 27.8 cps. As shown in FIG. 2, both the 25% and 50% substitution runs with CellGuard[™]OP produced higher viscosity results of 28.6 cps and 29.3 cps respectively after the E_{op} stage. These results indicate that CellGuard[™]OP serves a dual role as a peroxide activator and cellulose protector. In a conventional E_{op} system where NaOH and MgSO₄ are utilized, CellGuard[™]OP Mg(OH)₂ can reduce the NaOH consumption and eliminate MgSO₄. As seen in FIG. 2, the control sample's final viscosity was 16.5 cps, the 25% and 50% substitution samples with CellGuard[™]OP produced pulps with respective viscosities of 17.5 cps and 18.6 cps. By utilizing CellGuard[™]OP Magnesium Hydroxide in the E_{op} stage, a one to two point increase in pulp viscosity over the conventional E_{op} stage was achieved.

Fiber strength was maintained in both CellGuard $^{\text{TM}}$ OP substitution cases as shown in Figure 3. Wet zero-span tensile strength for all cases ranged from 10.9 - 11.0 km for the E_{op} stage, 10.2 - 10.6 for the D_1 stage, and 10.3 - 10.4 km for the D_2 stage.

High chemical oxygen demand (COD) is generated in the E_{op} stage where the most of the extraction occurs (see FIG. 4). Partially substituting the NaOH charge with a weak alkali such as $Mg(OH)_2$ reduces the organic loading in the effluent from the E_{op} stage. The higher substitution rate with CellGuard OP

yielded a noticeable reduction in COD when compared to the control sample. The control sample generated 4635 mg/L COD versus 4105 mg/L COD for the 50% substitution case, which represents an 11% reduction. Lower COD loading can contribute to reduced effluent treatment costs downstream.

By employing partial substitution of CellGuard $^{\mathsf{TM}}$ OP Magnesium Hydroxide Slurry for caustic soda and eliminating magnesium sulfate in the E_{op} stage, a strong alkali is present to facilitate lignin removal while a mild alkali is added to promote peroxide bleaching and cellulose protection. CellGuard $^{\mathsf{TM}}$ OP can replace up to 50% of the caustic soda requirement in the E_{op} stage producing final pulp from the D_2 stage with similar brightness, permanganate number, and wet zero-span tensile strength as pulp bleached with a 100% caustic soda charge.

At 50% substitution of caustic soda, the use of CellGuard[™]OP improves the pulp viscosity by 12% and reduces the COD after the E_{op} stage by 11%. Since only 0.73 kg of magnesium hydroxide provides the equivalent amount of hydroxyl ions as 1 kg of caustic soda, CellGuard[™]OP reduces bleaching costs in many cases. At no added cost beyond the amount required for caustic soda replacement, CellGuard[™]OP also eliminates the need for magnesium sulfate for further reduction in chemical costs.

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TABLE II RESULTS OF PARTIAL SUBSTITUTION OF CAUSTIC SODA WITH MAGNESIUM HYDROXIDE SLURRY IN THE EOP STAGE OF A DEopDepD BLEACH SEQUENCE

		Stag e	Chemical (% on pulp) ¹	Time (min)	Temp (°C)	Pressure (kPa)	End pH	ISO Bright-ness (%)	Viscosity(cp)	X No.	Wet Zero-Span (km)	COD (mg/l)
	Brown- stock							26.9	48.0	(29.2 as kappa)	12.5	
	D_0 Stage	D_{0}	0.22 kf (2.44% ClO₂)	45	60		2.3 ²	35.9		7.4 (11.9 as kappa)		
1	Control NaOH +	Eop	0.5% H ₂ O ₂ 1.7% NaOH 0.1% MgSO ₄ 0% Mg(OH) ₂	60	70	138 kPa O ₂ for 20 min, then atm	11.3	62.1	27.8	3.1	10.9	4635
tion time time	MgSO ₄	D_1	1.2% ClO ₂	180	80		2.3	80.2	21.4	1.1	10.2	1352
i di		Ep	0.15% H ₂ O ₂ 0.5 % NaOH	40	70		11.4	86.0				
100		D_2	0.6% ClO ₂	100	80		3.3	90.8	16.5	0.6	10.3	176
	25% Substitution	Eop	0.5% H ₂ O ₂ 1.275% NaOH 0.31% Mg(OH) ₂	60	70	138 kPa $O_2 \text{ for}$ 20 min , then atm	10.1	60.1	28.6	3.4	10.8	4555
	CellGuard [™] in Eop	D_1	1.2% ClO ₂	180	80		2.3	78.9	22.1	1.3	10.3	1326
.		Ер	0.15% H ₂ O ₂ 0.5 % NaOH	40	70		11.4	85.3				
		D_2	0.6% ClO ₂	100	80		3.3	90.5	17.5	0.6	10.2	
	50% Substitution	Eop	0.5% H ₂ O ₂ 0.85% NaOH 0.62% Mg(OH) ₂	60	70	138 kPa $O_2 \text{ for}$ 20 min , then $a \text{tm}$	9.3	59.7	29.3	3.5	11.0	4105
	CellGuard [™] in Eop	D_1	1.2% ClO ₂	180	80		2.3	76.3	22.0	1.4	10.6	1420
	in Eop	Еp	0.15% H ₂ O ₂ 0.5% NaOH	40	70		11.3	83.9				j ded Ž
		D_2	0.6% ClO ₂	100	80		3.2	89.9	18.6	0.7	10.4	184

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% on oven-dried pulp
 After washing, pH was 7.5
 All experiments were conducted at 12% pulp consistency.

 E_{op} - D_1 - E_p - D_2 Stages (Table III)-Standard conditions were employed for the D₁ and D₂ stages of bleaching processes shown in Table III. In the experiments involving substitution of magnesium hydroxide for NaOH in the E_p stage, magnesium hydroxide was substituted for all of the magnesium sulfate and a portion of the NaOH (25%, 50%, 75% or 100%). The E_{op} stage employed a 50% substitution of magnesium hydroxide for NaOH, and 100% substitution for all of the magnesium sulfate, in all the bleaching experiments. The pulp and filtrate following each bleaching stage were tested for ISO brightness and end pH, respectively. The pH of the residual liquor was determined using a pH meter and appropriate buffer solutions to calibrate the pH meter. Pulp samples from the E_{op} , D₁, and D₂ stages were also tested for viscosity and K#. As seen in Table III, the final ISO brightness, viscosity and K# of the bleached chemical pulp of the process of the present invention is comparable or greater than the the final ISO brightness, viscosity and K# of bleached chemical pulp which is bleached with the same total amount of an E_p aqueous bleaching solution comprising said peroxide compound and sodium hydroxide, but in the absence of magnesium hydroxide.

Table III. RESULTS OF SUBSTITUTION OF CAUSTIC SODA AND MAGNESIUM SULFATE WITH MAGNESIUM HYDROXIDE SLURRY

In E_{op} and E_P Stages of a DE_{op} DE_pD Bleach Sequence

	Stage	Chemical %	Time (min)	T E M p	Pressure (psig)	Kappa	K# 25 ml	ISO Bright- ness %	Vis- cos- ity cp
BS	Brownstock					30.4		26.1	51.9
D After washing To 7.5 pH	D	0.22kf (2.54% CIO ₂)				13.7	8.6	34.3	48.2
CONTROL NaOH +	E _{op} 100% OH- from NaOH	0.5%H ₂ O ₂ 1.7% NaOH 0.1% MgSO ₄ 0% Mg (OH) ₂	60	70	138Kpa 0 ₂ for 20 min. then atm		3.5	61.6	41.9
MgSO ₄ Sequence	D1	1.2% CIO ₂	180	80			1.3	79.6	29.8
E _{op} & E _p stage NaOH only	E _p 100% OH- from NaOH	0.15%H ₂ O ₂ 0.48% NaOH 0% Mg (OH) ₂	40	70				86.4	
	D2	0.6% CIO ₂	100	80			0.6	90.7	22.0
Mg(OH) ₂ Substitution Sequence	E _{op} 50% OH- from Mg(OH) ₂	0.5%H ₂ O ₂ 0.85% NaOH 0.62% Mg (OH) ₂	60	70	138Kpa 0 ₂ for 20 min. then atm		4.0	54.9	42.6
Eop	D1	1.2% CIO ₂	180	80	,		1.6	74.9	32.9
50% Substitution E _p Varying	E _p Control	0.15%H ₂ O ₂ 0.48% NaOH 0% Mg (OH) ₂	40	70				84.0	
Substitution	D2	0.6% CIO ₂	100	80			0.7	90.3	24.6

	TE T		40	70		83.6	
	E _p 25% OH- from Mg(OH) ₂	0.15%H ₂ O ₂ 0.36% NaOH 0.09% Mg	-				
	D2	(OH) ₂	100	80	0.7	90.2	24.6
	E _p 50% OH-	0.6% CIO ₂	40	70		83.1	
	50% OH- from Mg(OH) ₂	0.15%H ₂ O ₂ 0.24% NaOH 0.18% Mg					
Cont-	D2	(OH) ₂	100	80	0.8	89.9	25.2
		0.6% CIO ₂					
Mg(OH) ₂ Substitution	E _p 75% OH- from Mg(OH) ₂		40	70		81.5	
Cont- $Mg(OH)_2$ Substitution Sequence E_{op} 50% Substitution E_p Varying	D2	0.15%H ₂ O ₂ 0.12% NaOH 0.26% Mg (OH) ₂	100	80		89.5	25.3
Substitution En	E _p 100% OH- from Mg(OH) ₂	0.6% CIO ₂	40	70		78.8	
Varying Substitution	D2	0.15%H ₂ O ₂ 0% NaOH 0.35% Mg (OH) ₂	100	80	0.8	88.6	24.0
	,	0.6% CIO ₂					